THE PROPERTIES OF AMORPHOUS CARBON NITRIDE FILMS GROWN BY NEWLY DEVELOPED SURFACE WAVE MICROWAVE PLASMA CVD AFTER HEAT-TREATED AT VARIOUS ANNEALING TEMPERATURES

M. Rusop, T. Soga and T. Jimbo

Department of Environmental Technology and Urban Planning,

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

S. Adhikari, A.M.M. Omer, S. Adhikary, H. Uchida and M. Umeno

Department of Electronic Engineering, Faculty of Engineering,

Chubu University, Matsumoto-cho1200, Kasugai 487-8501, Japan

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Abstract

We have studied the effects of annealing temperature (AT) on the properties of amorphous carbon nitride (a-CN_x) thin films grown at room temperature (RT) on quartz substrates by surface wave microwave plasma chemical vapor deposition (SWMP-CVD) using camphor alcohol gas as carbon plasma sources. The thickness, optical, bonding, structural and electrical properties of the as-grown (RT) and heat-treated in range from 100 to 500 ^{o}C of a-CN_x films were measured and compared. The film thickness is decreased rapidly with increasing AT above 350 ^{o}C. The wide range of optical absorption coefficient characteristics is observed depending on the AT. The optical band gap of as-grown a-CN_x films is found to be approximately 2.8 eV, after which it gradually decreased down to 2.5 eV for the films heat-treated at 300 ^{o}C and beyond that it decreased rapidly down to 0.9 eV at 500 ºC of AT. Visible-Raman Spectroscopy (Raman) has revealed the amorphous structure of as-grown a-CN_x films and, the growth of nanocrystallinity of a-CN_x films upon increase of AT. Raman and Fourier transform infrared spectroscopy (FTIR) analyses respectively shown the structural and composition of the films can be tuned by optimizing the AT. The change of optical, bonding, structural and electrical properties of SWMP-CVD grown a-C:N films with higher AT was attributed due to the fundamental changes in the bonding and band structure of the a-C:N films. All of the measurements were carried out using standard measurement techniques.

RESULTS AND DISCUSSIONS

Figure 1 displays the evolution of the RS in the range 1000 to 1800 cm^{-1} of as-grown and heat-treated a-CN_x films. The shape and position of the spectra are almost unchanged up to 150 ^{o}C, after which it gradually grows splitter in to sub band with higher AT. The G peak shifts to higher wave number and become narrower with increase of AT higher than 300 ^{o}C. The experimental data were best fitted with the accuracy factor is about 0.95 by two peaks considering 2 Gaussian line shapes into two Raman bands of D and G peaks, and the linear background and the plot of this kind of RS for the as-grown and heat-treated a-CN_x films. It is clear that the broad band resulted from the a-C:N film (grown at 25 ^{o}C) gradually splitted into two peaks (commonly known as D and G peaks) with the increase of AT, may be due to the progressive crystallization upon increase of AT. The RS shows a similar trend to those observed by Dillon et al. [1] and Mominuzzaman et al. [2] in their heat treatment experimental of C films. This indicates that these films consisted of a disordered graphite matrix with some sp^3- hybridized C states [3].

The electrical resistivity (ρ) was measured at room temperature (RT) by a 4-point probe resistance measurement method, the usual way for high resistance measurement. The ρ values for each film were the average of measurements made at different positions on the film surface. Figure 2 shows the ρ values of as-grown a-C:N film measured to be around 7.5 x 10^5 (Ω-cm) gradually decreases with higher AT to 6.1 x 10^5 (Ω-cm) at 100 ^{o}C. As AT increases, the ρ decreases up to 3.5 x 10^5 (Ω-cm) at 200 ^{o}C. At higher AT, as can be seen in figure 6 and figure 10, both of the E_g and ρ are gradually decreases up to 2.3 eV and 2.3 x 10^5 (Ω-cm) at 300 ^{o}C, respectively. The variation of the optical and electrical properties can be related to interstitial doping of N in a-C films through modifications of C-N bonding configurations by rearranging of N atoms upon increase of AT. However with further increase of AT above 300 °C, both E_g and ρ are drastically decreases up to 0.9 eV and 1.5 x 10^4 (Ω-cm) at 500 °C, respectively. This is probably due to the graphitization of the a-C:N films. Perhaps the doping of N accompanied by increase of AT above 300 °C increases crystallinity and subsitutional doping of N thereby sharply decreases resistivity. These phenomena also supported by the Raman and FTIR spectroscopy measurements.

Details of the experimental results and discussions will be presented during the conference presentation.

Conclusions

We have grown nitrogenated amorphous carbon (a-CN_x) films by surface wave microwave plasma chemical vapor deposition (SWMP-CVD) method and the effects of annealing temperature (AT) in range from 100 to 500 °C has been studied in details. The thickness, optical, structural and bonding properties of the as-grown and heat-treated a-CN_x films were measured and compared. The film thickness is decreased rapidly with increasing AT above 300 °C. The optical band gap of the as-grown a-CN_x films was found to be approximately 2.8 eV, remained almost constant until 300 °C, and beyond that it decreased monotonically up to 0.9 eV at 500 °C. Visible-Raman scattering analyses revealed the amorphous structure of as-grown a-CN_x films and, the growth of nanocrystallinity of a-CN_x films upon increase of AT. We found that, both the sp^2 and sp^3- hybridized C atoms can be bound to the N atoms in the a-CN_x films. The FTIR spectroscopy measurements also have shown that the structural and composition of the films can be tuned by optimizing the AT. The change of bonding, structural, optical and electrical properties of SWMP-CVD grown a-CN_x films with higher AT was attributed due to the fundamental changes in the bonding and band structure of the films. The result shows it is possible to control the bonding, structural, optical band gap and electrical properties of SWMP-CVD grown a-C:N films by the annealing process for its possible application in various electronic devices.

REFERENCES

1. R.O. Dillon, J.A. Woollam, V. Katkanant, Phys. Rev. B Vol. 29, pages 3482 (1984).
2. S.M. Mominuzzaman, K.M. Krishna, T. Soga, T. Jimbo, M. Umeno, Carbon Vol. 38, pages 127 (2000).
3. Y.K. Yap, S. Kida, T. Aoyama, Y. Mori, T. Sasaki, Appl. Phys. Lett. Vol. 73, pages 7 (1998).

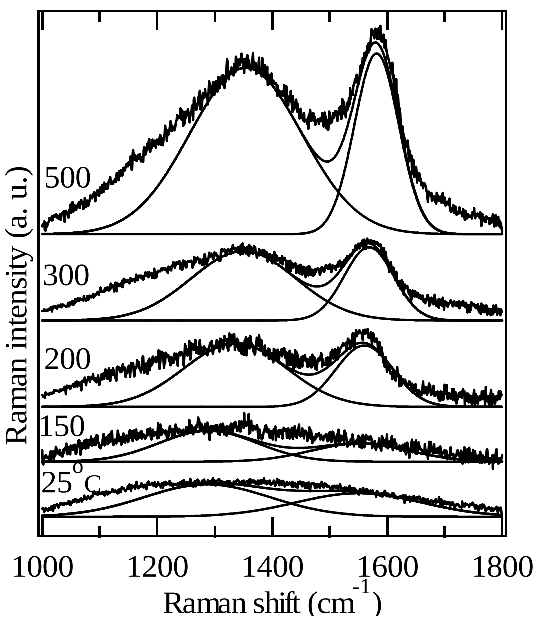

Figure 1: The Raman spectra of as-grown and a-C:N films heat-treated at various temperatures, and their images of deconvolution of Raman D and G peaks using 2 peaks of Gaussian lines. (Substrate: Quartz).

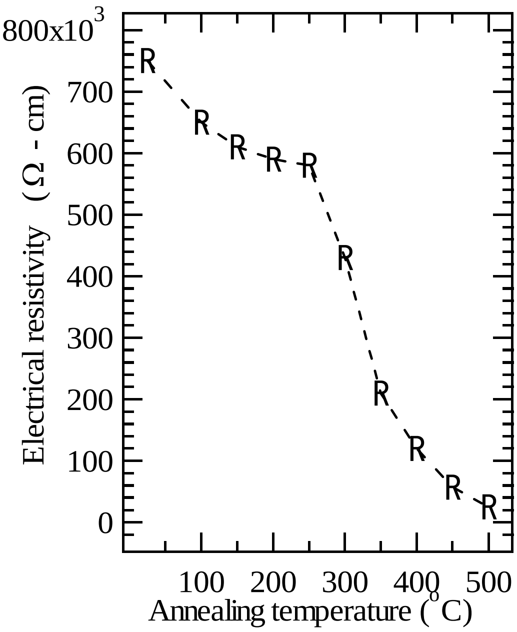

Figure 2: The variation of electrical resistivity of as-grown (25 °C) a-C:N film, and a-C:N films anneal-treated at various temperatures. (Substrate: Quartz).